PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C07F 9/6568, B01J 31/24, C07F 9/6571, C07C 45/50, 51/14, 67/38

A1

(11) International Publication Number: WO 98/42717

(43) International Publication Date: 1 October 1998 (01.10.98)

(21) International Application Number: PCT/EP98/01916

(22) International Filing Date: 25 March 1998 (25.03.98)

(30) Priority Data:
97302079.5 26 March 1997 (26.03.97) EP
(34) Countries for which the regional or international application was filed: GB et al.
97302958.0 30 April 1997 (30.04.97) EP
(34) Countries for which the regional or international application was filed: GB et al.

(71) Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL).

(72) Inventors: SUYKERBUYK, Jacoba, Catherina, Lucia, Johanna; Badhuisweg 3, NL-1031 CM Amsterdam (NL). DRENT, Eit; Badhuisweg 3, NL-1031 CM Amsterdam (NL). PRINGLE, Paul, Gerard; Cantocks Close, Bristol BS8 1TS (GB).

(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, GW, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: DIPHOSPHINES

(57) Abstract

The invention relates to a diphosphine of the following formula: $R^1{>}P{-}R^2{-}PR^3R^4$ wherein R^2 represents a covalent bridging group, R^1 represents a bivalent radical that together with the phosphorus atom to which it is attached is an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or a derivative thereof in which one or more of the carbon atoms are replaced by heteroatoms ("2-PA" group), and wherein R^3 and R^4 independently represent univalent radicals of up to 20 atoms or jointly form a bivalent radical of up to 20 atoms; to carbonylation catalysts obtainable by combining: (i) a metal cation selected from the groups (8, 9 or 10) of the Periodic Table of Elements, and (ii) the new diphosphine; and furthermore to a process for carbonylating unsaturated compounds in the presence of the carbonylation catalyst.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	**ES**	Spain	**LS**	Lesotho	**SI**	Slovenia
AM	Armenia	**FI**	Finland	**LT**	Lithuania	**SK**	Slovakia
AT	Austria	**FR**	France	**LU**	Luxembourg	**SN**	Senegal
AU	Australia	**GA**	Gabon	**LV**	Latvia	**SZ**	Swaziland
AZ	Azerbaijan	**GB**	United Kingdom	**MC**	Monaco	**TD**	Chad
BA	Bosnia and Herzegovina	**GE**	Georgia	**MD**	Republic of Moldova	**TG**	Togo
BB	Barbados	**GH**	Ghana	**MG**	Madagascar	**TJ**	Tajikistan
BE	Belgium	**GN**	Guinea	**MK**	The former Yugoslav	**TM**	Turkmenistan
BF	Burkina Faso	**GR**	Greece		Republic of Macedonia	**TR**	Turkey
BG	Bulgaria	**HU**	Hungary	**ML**	Mali	**TT**	Trinidad and Tobago
BJ	Benin	**IE**	Ireland	**MN**	Mongolia	**UA**	Ukraine
BR	Brazil	**IL**	Israel	**MR**	Mauritania	**UG**	Uganda
BY	Belarus	**IS**	Iceland	**MW**	Malawi	**US**	United States of America
CA	Canada	**IT**	Italy	**MX**	Mexico	**UZ**	Uzbekistan
CF	Central African Republic	**JP**	Japan	**NE**	Niger	**VN**	Viet Nam
CG	Congo	**KE**	Kenya	**NL**	Netherlands	**YU**	Yugoslavia
CH	Switzerland	**KG**	Kyrgyzstan	**NO**	Norway	**ZW**	Zimbabwe
CI	Côte d'Ivoire	**KP**	Democratic People's	**NZ**	New Zealand		
CM	Cameroon		Republic of Korea	**PL**	Poland		
CN	China	**KR**	Republic of Korea	**PT**	Portugal		
CU	Cuba	**KZ**	Kazakstan	**RO**	Romania		
CZ	Czech Republic	**LC**	Saint Lucia	**RU**	Russian Federation		
DE	Germany	**LI**	Liechtenstein	**SD**	Sudan		
DK	Denmark	**LK**	Sri Lanka	**SE**	Sweden		
EE	Estonia	**LR**	Liberia	**SG**	Singapore		

DIPHOSPHINES

The invention relates to novel diphosphines, novel carbonylation catalysts and a process for the carbonylation of unsaturated compounds by reaction thereof with carbon monoxide and a coreactant in the presence of the novel carbonylation catalysts.

Carbonylation reactions are known in the art. For instance, in EP-A-0,495,547 several examples are disclosed wherein olefins are converted into (thio)esters, acids, anhydrides, and amides, etc., depending on the nature of the coreactant. Other examples on the synthesis of aldehydes; ketones; carboxylic acids; esters; amides and other carboxylic acid derivatives; lactones; lactams and related N-heterocycles as well as background references can be found in "Carbonylation" by Messrs H M Colquhoun, D J Thompson and M V Twigg (Plenum press 1991). Typically, the rate of reaction is in the order of up to several hundreds moles product per mol catalyst (based on the metal) per hour. In case of internal unsaturation, the rate of reaction is even several orders lower. In other words, either relatively large amounts of catalyst are required or prolonged reaction times are involved.

The present inventors set out to provide a more active carbonylation catalyst. Surprisingly, carbonylation catalysts with high activity have been found that are obtainable by combining:

(i) a metal cation selected from the groups 8, 9 or 10 of the Periodic Table of Elements, and

(ii) a diphosphine of the following formula

$$R^1\!>\!P-R^2-PR^3R^4$$

wherein R^2 represents a covalent bridging group, R^1 represents a bivalent radical that together with the phosphorus atom to which it is attached is an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or a derivative thereof in which one or more of the carbon atoms are replaced by heteroatoms, and wherein R^3 and R^4 independently represent univalent radicals of up to 20 atoms or jointly form a bivalent radical of up to 20 atoms. The diphosphines that may be used in the preparation of these carbonylation catalysts are believed to be novel too.

Tricyclo[3.3.1.1{3,7}]decane is the systematic name for a compound more generally known as adamantane. Therefore, the optionally substituted 2-phospha-tricyclo-[3.3.1.1{3,7}decyl group will be referred to as "2-PA" group (as in 2-phosphadamantyl group) throughout the specification.

Preferably, the 2-PA group is substituted on one or more of the 1, 3, 5 or 7 positions with a monovalent radical R^5 of up to 20 atoms. Typical examples of R^5 include methyl, trifluoromethyl, ethoxy, phenyl, and 4-dodecylphenyl. More preferably, the 2-PA group is substituted on each of the 1, 3, 5 and 7 positions, suitably with identical radicals R^5.

The 2-PA group has preferably additional heteroatoms other than the 2-phosphorus atom in its skeleton. Suitable heteroatoms are oxygen and sulphur atoms. Suitably, these heteroatoms are found in the 6, 9 and 10 positions.

The most preferred bivalent radical is the 2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxadamantyl group.

Each of the monovalent radicals R^3 and R^4 may independently be selected from (substituted) hydrocarbyl groups such as, for instance, methyl, phenyl, pyridyl, or

o,o-di(t-butoxy)phenyl, and (substituted) heterohydrocarbyl groups such as, for instance, trimethylsilyl or alkoxy groups. Alternatively, R^3 and R^4 may together form a bivalent radical, such as 1,6-hexylene, 1,3 or 1,4-cyclooctylene, etc. Preferably, R^3 and R^4 together form a 2-PA group, most preferably a bivalent radical identical to R^1.

The preferred ligands to be used in the carbonylation catalysts of the present invention are 1,2-P,P'-di(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo-[3.3.1.1{3.7}decyl)ethane (DPA2); 1,3-P,P'-di(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3.7}-decyl)propane (DPA3); 1,2-P,P'-di-perfluoro(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3.7}-decyl)ethane, 1,3-P,P'-di-perfluoro(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3.7}decyl)-propane, 1,2-P,P'-di-(2-phospha-1,3,5,7-tetra(trifluoromethyl)-6,9,10-trioxatricyclo[3.3.1.1{3.7}decyl)ethane and 1,3-P,P'-di-(2-phospha-1,3,5,7-tetra(trifluoromethyl)-6,9,10-trioxatricyclo[3.3.1.1{3.7}decyl)propane, DPA3 being most preferred.

The ligand so defined can be prepared in a manner similar to the process for preparing the secondary phosphine 1,3,5,7-tetramethyl-2,4,8-trioxa-6-phospha-adamantane disclosed in chapter 3 of "PRECIOUS METAL COMPLEXES OF SOME NOVEL FUNCTIONALISED SECONDARY AND TERTIARY PHOSPHINES" by Ms. Joanne H Downing (theses submitted to the University of Bristol on November 1992). For instance, DPA3 is prepared by adding 2,4-pentanedione to 1,3-diphosphinopropane. Asymmetric ligands may be prepared using, for instance, a diphosphine having a tertiary phosphino group and a primary phosphino group. Alternatively, they may be prepared by coupling a secondary 2-phospha-tricyclo[3.3.1.1{3,7}decane with

another secondary monophosphine or by other processes known in the art. Substituted ligands can, for example, be made using substituted 2,4-pentanediones such as perfluoro-2,4-pentanedione or 1,1,1,5,5,5-hexfluoro-2,4-pentanedione in the reaction with the phosphine.

According to the present IUPAC notation, group 8, 9 and 10 metal cations are cations of Fe, Ru, Os; Co, Rh, Ir and Ni, Pd, and Pt, respectively. These cations, as is illustrated in "Carbonylation", may each be used in the various carbonylation reactions.

Group 9 metal cations, and Group 10 metal cations (referred to in the older literature as the platinum group metal cations) have been found to provide particularly good results when used in the novel catalyst of the present invention.

Suitable sources for the metal cations may be found in "Carbonylation" and will form no problem to the person skilled in the art. Likewise, the preparation of the catalyst system (actually a precursor, the active species formed in-situ may be slightly different from that of the precursor here disclosed) follows the general recipe disclosed in the thesis by Ms J H Downing.

The catalyst systems may be used in the various carbonylation reactions described in EP-A-0,495,547 and in "Carbonylation". They particularly excel in respect of the reaction rate when applied in the additive carbonylation of unsaturated compounds, notably of ethylenically unsaturated compounds. The latter reaction, here shown for an alpha-olefin, proceeds according to the following reaction:

$RCH{=}CH_2 + CO + HY \rightarrow RCH_2CH_2COY$; Y = H, OH, OR, NR_2, etc.

The additive carbonylation of internal olefins is similar. However, due to its high isomerisation activity,

the products typically resemble those of the reaction with the corresponding alpha-olefin.

In other words, the catalyst systems may be used in "hydroformylation reactions", "hydrocarboxylation reactions", "hydroesterification reactions", "hydroamidation reactions", etc.

It will be understood that in such carbonylation reactions coreactants, solvents, etc. may be used. Besides, various anions may be used as counter-ion to the metal cation. Examples thereof include anions that are the conjugated base of acids having a pKa (measured at 18 °C in water) of less than 6, preferably less than 4. The anions derived from these acids do not or only weakly co-ordinate with the metal cation, by which is meant that little or no covalent interaction occurs between the anion and the cation. Catalysts based on these anions exhibit a good activity.

Suitable anions include anions derived from Bronsted acids, such as from phosphoric acid and sulphuric acid, and in particular from sulphonic acids and (halogenated) carboxylic acids, such as trifluoroacetic acid, 2,6-dichlorobenzoic acid, and 2,6-bis(trifluoromethyl)benzoic acid or trifluoroacetic acid, etc. Anions derived from sulphonic acids are particularly preferred, for example methanesulphonic acid, trifluoromethanesulphonic acid, tert-butanesulphonic acid, p-toluenesulphonic acid and 2,4,6-trimethylbenzenesulphonic acid.

Also, complex anions are suitable, such as the anions generated by a combination of a Lewis acid such as BF3, $B(C_6F_5)_3$, $AlCl_3$, SnF_2, $Sn(CF_3SO_3)_2$, $SnCl_2$ or $GeCl_2$, with a protic acid, preferably having a pKa of less than 5, such as a sulphonic acid, e.g. CF_3SO_3H or CH_3SO_3H or a hydrohalogenic acid such as HF or HCl, or a combination

of a Lewis acid with an alcohol. Examples of such complex anions are BF_4^-, $SnCl_3^-$, $[SnCl_2.CF_3SO_3]^-$ and PF_6^-.

The carbonylation reaction is conveniently carried out at moderate temperatures. Accordingly, the process is suitably carried out at a temperature in the range of 30 to 200 °C, preferred temperatures being in the range of 50 to 180 °C. The reaction pressures may also vary widely. For instance, the reaction can be carried out with pressures in the range of 1 to 200 bar gauge, pressures in the range of 5 to 60 barg being preferred.

Carbon monoxide is preferably supplied in molar excess over the unsaturated compound and the coreactant "YH". In addition, the unsaturated compound and the coreactant are suitably supplied in a molar ratio within the range of 10:1 to 1:10, preferably within the range of 5:1 to 1:5, more preferably within the range of 2:1 to 1:2.

The quantity in which the catalyst system is used, is not critical and may vary within wide limits. Usually amounts in the range of 10^{-8} to 10^{-1}, preferably in the range of 10^{-7} to 10^{-2} mole atom of metal per mole of unsaturated compound are used.

For the preparation of the catalyst systems of the invention, the amount of ligand is generally applied in some excess of the amount of the metal cation, expressed as moles of ligand per mole atom of the cation. Typically the amount of ligand is selected such that per mole atom of the cation 0.5 to 10 moles of ligand are present. However, for the preferred catalyst system the active species is believed to be based on an equimolar amount of bidentate ligand per mole cation. Thus, the molar amount of bidentate ligand per mole of cation is preferably in the range of 1 to 3, more preferably in the range of 1 to 2. In the presence of oxygen, slightly higher amounts may

be beneficial. The amount of the anion source may range from 0.5 to 15, preferably from 1 to 8 moles per mole of cation.

In the process of the invention, the starting materials and the formed carbonylation products may act as reaction diluent. Hence, the use of a separate solvent is not necessary. Conveniently, however, the carbonylation reaction may be carried out in the additional presence of a solvent. As such, saturated hydrocarbons such as, e.g., paraffins and isoalkanes are recommended and furthermore ethers such as 2,5,8-trioxanonane (diglyme), diethylether and anisole; sulphones such as sulpholane, and aromatic hydrocarbons such as toluene.

The unsaturated compound may have one or more unsaturated bonds and is preferably an olefin having from 2 to 30 carbon atoms per molecule. The unsaturated bond(s) may be internal or terminal, the catalyst being particularly advantageous in the conversion of internal olefins. Particularly preferred are olefins having from 2 to 22 carbon atoms per molecule, such as ethene, propene, 1- or 2-butene, 1- or internal hexene, 1 or internal octene, diisobutylene, triisobutylene, tripropylene, internal decene, internal C_{14} olefins, and internal C_{15}-C_{18} olefins.

In the unsaturated compound one or more hydrogen atoms may have been substituted by other atoms, such as halogen atoms or by groups of atoms, such as hydroxyl groups, cyano groups, such as methoxy or ethoxy groups, or amino groups such as dimethyl- and diethyl-amino groups.

Another preferred category of unsaturated compounds, consists of unsaturated esters of carboxylic acids and esters of unsaturated carboxylic acids. For example, the starting material may be a vinyl ester of a carboxylic acid such as acetic acid or propanoic acid, or it may be

an alkyl ester of an unsaturated acid, such as the methyl or ethyl ester of acrylic acid or methacrylic acid.

A further preferred category of unsaturated compounds, consists of cycloalkadienes, which will ordinarily refuse carbonylation. For example, the starting material may be dicyclopentadiene or norbornadiene, to give diesters, diamides or diacids, etc., which may find use as monomer in polymerization reactions.

Suitable coreactants in the additive carbonylation process of the invention include compounds comprising a nucleophilic moiety and a mobile hydrogen atom.

Preferred nucleophilic compounds include: molecular hydrogen, water and alcohols, e.g., monohydric alcohols, such as methanol, ethanol, isopropanol and 1-butanol, and polyhydric alcohols, such as ethyleneglycol, 1,4-butanediol and glycerol; thiols; primary or secondary (poly-) amines or amides, such as diethylamine, N,N-dimethyl ethylenediamine; aromatic alcohols and carboxylic acids, for example acetic acid, pivalic acid and propanoic acid. Molecular hydrogen, monohydric alcohols having from 1 to 6 carbon atoms per molecule and dihydric alcohols having from 2 to 6 carbon atoms per molecule are preferred.

1-Butanol, methanol and 1,4-butanediol are especially preferred. The use of these compounds as coreactants enables the production of valuable carbonylation products, such as methyl propanoate, butyl propanoate and 1,4-diacyloxy butanes. These compounds are of commercial interest and may be used as solvents and in flavouring compositions and perfumes.

Another preferred class of coreactants is composed of alkylphenols, wherein one or more alkyl groups of up to 30, typically 6 to 22 carbon atoms are attached to the phenol molecule. Additive carbonylation with these coreactants produces alkylphenyl esters that may find use

as synthetic lubricants in industrial application, but in particular in automotive engines.

The invention will now be further described in the following examples, however, without restricting its scope. All experiments were carried out in a magnetically stirred 250 ml autoclave unless otherwise indicated. The abbreviations used in the Tables have the following meanings:

DPA2 = 1,2-P,P'-di(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3.7}decyl)ethane

DPA3 = 1,3-P,P'-di(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3.7}decyl)propane

MSA = methanesulphonic acid

Example 1 (Synthesis of the ligands)

4.63 Mmol diphosphinopropane was added to a solution of 27.8 mmol 2,4-pentanedione in 20 ml 5M HCl. After 1 hr stirring a white solid began to precipitate. The reaction mixture was stirred for a further 24 hrs, and then the volatile components were removed to leave a white, air-stable solid product. The product was washed with water (6x 20 ml), dissolved in 20 ml dichloromethane and dried over magnesium sulphate, This solution was filtered and concentrated under vacuum to 1 ml. 10 ml pentane was added to precipitate the purified product, which was then recovered. (0.75 g, 34% yield).

^{1}H NMR (400 MHz, in CD_2Cl_2), d 1.18 (6H, s), d 1.22 (18H, s), d 1.4-1.9 (m, 14H); ^{31}P NMR (162 MHz): d -30.0, -30.8 ppm; mass spectrum showed m/e 472 (M+). These data confirm the nature of the product.

DPA2 was prepared in an identical manner, however, employing diphosphinoethane instead of diphosphinopropane.

Example 2 (Carbonylation)

The autoclave was charged with 50 ml of methanol, 0.1 mmol of palladium(II) acetate, 0.15 mmol of DPA3, and 0.2 mmol of MSA. After being flushed, the autoclave was pressurised with carbon monoxide and ethene to a partial pressure of 30 bar and 20 bar respectively. Next, the reactor was sealed. The contents of the autoclave were heated to a temperature of 90 °C and maintained at that temperature for 0.25 hours. After cooling, a sample was taken from the contents of the autoclave and analysed by Gas Liquid Chromatography.

Ethene was fully converted with 100% selectivity into methyl propanoate at an average rate of 8000 mole per mole Pd per hour (mol/mol.hr).

Example 3

Example 2 was repeated, however using 10 ml water and 40 ml of diglyme as reactant/solvent and a process temperature of 110 °C. The autoclave was cooled after 2 hours.

Ethene was fully converted with 100% selectivity into propanoic acid at an average rate of 1500 mol/mol.hr.

Example 4

Example 2 was repeated, however using 30 ml propene as olefin and a process temperature of 100 °C.

Propene was fully converted with 78% selectivity into methyl butanoate and 22% selectivity into methyl 2-methylpropanoate at an average rate of 5000 mol/mol.hr.

Example 5

Example 2 was repeated, however using 20 ml of an alpha-C_{14} olefin feed. The autoclave was cooled after 3 hours.

The alpha-olefins were converted for 95% with 80% selectivity into linear methyl esters at an average rate of 250 mol/mol.hr.

Example 6

Example 2 was repeated, however using 20 ml of an internal-C_{14} olefin feed, at a process temperature of 115 °C, and at a carbon monoxide pressure of 10 bar. The autoclave was cooled after 5 hours.

The internal olefins were converted for 93% with 78% selectivity into linear methyl esters at an average rate of 120 mol/mol.hr.

Comparative Example A

Example 6 was repeated, however using 1,3-bis(di-tert-butylphosphino)propane as ligand, and at a carbon monoxide pressure of 10 and 30 bar, respectively. The autoclave was cooled after 10 hours.

The internal olefins were converted for only 10% with 75% selectivity into linear methyl esters at an average rate of 5 mol/mol.hr.

Example 7

Example 2 was repeated, however using 10 ml methyl 3-pentenoate as unsaturated compound, at a process temperature of 115 °C and at a carbon monoxide pressure of 15 bar. The autoclave was cooled after 6 hours.

Methyl 3-pentenoate was fully converted with 84% selectivity into linear dimethyl esters at an average rate of 100 mol/mol.hr.

Example 8

Example 2 was repeated, however using 0.1 mmol of platinum(II) acetylacetonate, 0.12 mmol of DPA3, and 0.25 mmol of MSA. Besides, the contents of the autoclave were heated to 125 °C. The autoclave was cooled after 3 hours.

Ethene was fully converted with 100% selectivity into methyl propionate at an average rate of 500 mol/mol.hr.

Comparative Example B

Example 8 was repeated, however using 1,3-bis(di-tert-butylphosphino)propane as ligand.

Methyl propionate was now formed at an average rate of only 10 mol/mol.hr.

Example 9 (hydroformylation)

The autoclave was charged with 50 ml diglyme, 0.1 mmol rhodium dicarbonyl acetylacetonate, and 0.12 mmol of DPA3. After being flushed, the autoclave was charged with 15 ml propene and pressurised with carbon monoxide and hydrogen to a partial pressure of 25 bar and 25 bar each. Next, the reactor was sealed. The contents of the autoclave were heated to a temperature of 80 °C and maintained at that temperature for 0.25 hours. After cooling, a sample was taken from the contents of the autoclave and analysed by GLC.

Propene was fully converted into a mixture of butanal and 2-methylpropanal (mole ratio 48:52) at an average rate of 4000 mol/mol.hr.

Example 10

Example 9 was repeated, however using 0.1 mmol of DPA2.

Propene was now fully converted into a mixture of butanal and 2-methylpropanal (mole ratio 49:51) at an average rate of 5000 mol/mol.hr.

Example 11

Example 9 was repeated, however using 10 ml of vinyl acetate instead of propene, 50 ml of toluene instead of diglyme and 0.2 mmol of DPA3. Besides, the autoclave was heated to a temperature of 115 °C.

Vinyl acetate was fully converted into a mixture of 1-formylethyl acetate and 2-formylethyl acetate (mole ratio 10:1) at an average rate of 5000 mol/mol.hr.

CLAIMS

1. A diphosphine of the following formula

$R^1>P-R^2-PR^3R^4$

wherein R^2 represents a covalent bridging group, R^1 represents a bivalent radical that together with the phosphorus atom to which it is attached is an optionally substituted 2-phospha-tricyclo[3.3.1.1{3,7}]decyl group or a derivative thereof in which one or more of the carbon atoms are replaced by heteroatoms ("2-PA" group), and wherein R^3 and R^4 independently represent univalent radicals of up to 20 atoms or jointly form a bivalent radical of up to 20 atoms.

2. A diphosphine as claimed in claim 1, wherein the 2-PA group is substituted on one or more of the 1, 3, 5 or 7 positions with a monovalent radical R^5 of up to 20 atoms.

3. A diphosphine as claimed in claim 2, wherein R^5 is a radical selected from methyl, trifluoromethyl, ethoxy, phenyl, and 4-dodecylphenyl.

4. A diphosphine as claimed in any one of claims 1 to 3, wherein the 2-PA group is substituted on each of the 1, 3, 5 and 7 positions, preferably with identical radicals R^5.

5. A diphosphine as claimed in any one of claims 1 to 4, wherein the 2-PA group has oxygen and or sulphur atoms in its skeleton, preferably in the 6, 9 and 10 positions.

6. A diphosphine as claimed in any one of claims 1 to 5, wherein the 2-PA group is a 2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxadamantyl group.

7. A diphosphine as claimed in any one of claims 1 to 6, wherein R3 and R4 together form a 2-PA group, preferably a bivalent radical identical to R^1.

8. A diphosphine as claimed in claim 1, wherein the ligand is selected from 1,2-P,P'-di(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3.7}decyl)-ethane (DPA2); 1,3-P,P'-di(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3.7}decyl)propane (DPA3); 1,2-P,P'-di-perfluoro(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3.7}decyl)ethane, 1,3-P,P'-di-perfluoro(2-phospha-1,3,5,7-tetramethyl-6,9,10-trioxatricyclo[3.3.1.1{3.7}decyl)propane, 1,2-P,P'-di-(2-phospha-1,3,5,7-tetra(trifluoromethyl)-6,9,10-trioxatricyclo[3.3.1.1{3.7}decyl)ethane and 1,3-P,P'-di-(2-phospha-1,3,5,7-tetra(trifluoromethyl)-6,9,10-trioxatricyclo[3.3.1.1{3.7}decyl)propane, DPA3 being most preferred.

9. A carbonylation catalyst obtainable by combining:

(i) a metal cation selected from the groups 8, 9 or 10 of the Periodic Table of Elements, and

(ii) a diphosphine as claimed in any one of claims 1 to 8.

10. A carbonylation catalyst as claimed in claim 9, wherein the metal cation is a group 9 metal cation or a group 10 metal cation, preferably Rh, Pd or Pt.

11. A process for the carbonylation of an unsaturated compound by reaction thereof with carbon monoxide and a coreactant, wherein a carbonylation catalyst is used as claimed in any one of claims 9 or 10.

12. A process as claimed in claim 11, wherein the unsaturated compound is ethylenically unsaturated compound of 2 to 30 carbon atoms per molecule.

13. A process as claimed in claim 12, wherein the ethylenically unsaturated compound is an alpha- or internal

olefin having from 2 to 22 carbon atoms per molecule, or a cycloalkadiene.

14. A process as claimed in any one of claims 11 to 13, wherein the coreactant is molecular hydrogen, monohydric alcohols having from 1 to 6 carbon atoms per molecule, dihydric alcohols having from 2 to 6 carbon atoms per molecule and alkylphenols.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 98/01916

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07F9/6568 B01J31/24 C07F9/6571 C07C45/50 C07C51/14
C07C67/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07F B01J C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 495 547 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 22 July 1992 cited in the application see the whole document ---	1-14
Y	WO 95 03269 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 2 February 1995 see the whole document ---	1-14
Y	US 3 527 818 A (RONALD F. MASON) 8 September 1970 see the whole document ---	1-14
A	GB 949 513 A (AMERICAN CYANAMID CO.) 12 February 1964 -----	

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
28 August 1998	04/09/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Beslier, L

1

INTERNATIONAL SEARCH REPORT

Internatic Application No
PCT/EP 98/01916

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 495547 A	22-07-1992	CA 2059233 A	16-07-1992
		CA 2059236 A	16-07-1992
		CN 1063277 A	05-08-1992
		DE 69204691 D	19-10-1995
		DE 69204691 T	11-04-1996
		DE 69210054 D	30-05-1996
		DE 69210054 T	12-12-1996
		EP 0495548 A	22-07-1992
		ES 2088082 T	01-08-1996
		ES 2077337 T	16-11-1995
		JP 5058949 A	09-03-1993
		JP 4334340 A	20-11-1992
		SG 45352 A	16-01-1998
		US 5210280 A	11-05-1993
WO 9503269 A	02-02-1995	CN 1127501 A	24-07-1996
		DE 69409651 D	20-05-1998
		DE 69409651 T	06-08-1998
		EP 0710224 A	08-05-1996
		ES 2114698 T	01-06-1998
		JP 9500384 T	14-01-1997
US 3527818 A	08-09-1970	BE 690123 A	24-05-1967
		DE 1593466 A	23-07-1970
		FR 1502250 A	02-02-1968
		GB 1127965 A	
		JP 49038278 B	16-10-1974
		NL 6616540 A,B	29-05-1967
		US 3401204 A	10-09-1968
GB 949513 A		US 3050531 A	21-08-1962
		US 3026327 A	20-03-1962